# Thermophysical and thermal optical properties of vanadium by millisecond calorimetry between 300 and 1900 $\,\mathrm{K}$

A. Stanimirović, G. Vuković and K. Maglić Institute of Nuclear Sciences "Vinča"
P.O. Box 522, 11001 Belgrade, Yugoslavia

## Abstract

A variant of millisecond resolution pulse calorimetry in use at the Institute of Nuclear Sciences "Vinča" since 1983, involves measuring specific heat and electrical resistivity of electrical conductors from room temperature to 2500 K, and hemispherical total emittance and normal spectral emittance from about 1300 K to the same maximum operating temperature. The method was applied successfully to different materials: pure metals, ferrous and nickel-base alloys, reactor materials, refractory metals, in thermal characterization of candidates for thermophysical property standard reference materials etc. Paper presents and discusses new data obtained in the study of thermophysical and thermal optical properties of vanadium.

KEY WORDS:

electrical conductors; electrical resistivity; hemispherical total emittance; high temperatures; normal spectral emittance; refractory metals; specific heat.

## 1. INTRODUCTION

Vanadium is the last in the group of refractory metals whose thermophysical and thermal optical properties have been studied at the Institute of Nuclear Sciences "Vinča" by millisecond resolution pulse calorimetry. Other metals, tungsten [1], niobium [2], molybdenum [3] and tantalum (not yet published) were investigated before. Vanadium is a metal important in metallurgical processes. Its study was also interesting as very few recent data could be found either in the data reference books, or in the THERSYST data bank.

## 2. EXPERIMENTAL

A sample of vanadium in the form of a rod 2 mm in diameter 200 mm long, with nominal purity of 99.8+% (Goodfellow)<sup>2</sup>, was used in the millisecond resolution pulse calorimetry experiments as received, without further thermal treatment. The method, apparatus and measurement uncertainties have been described previously [4,5].

Specific heat and electrical resistivity were measured using 0.05 mm PtRh10%/Pt thermocouples. DC pulses ranging from 300 to 600 A delivered by two heavy duty 12 V batteries connected in series resulted in heating rates of 2000 to 2800 K s<sup>-1</sup>.

<sup>2</sup> Typical analysis given by the manufacturer is: Ag 1, Al 2, Ca <1, Cr 15, Cu <1, Fe 70, Mg <1, Mn 1, Si 300 (ppm)

THERSYST is a name of a thermophysical properties data bank for solid materials developed and operated by the University of Stuttgart-IKE, Stuttgart, Germany

Experiments with parallel pyrometric temperature measurements gave in addition hemispherical total emittance and normal spectral emittance, beside specific heat and electrical resistivity. Experimental procedure is described in detail in [5].

### 3. RESULTS

In order to increase statistical weight of the final resulting functions, specific heat and electrical resistivity were measured in seven experiments, with the maximum temperatures of different experiments ranging between 1898 and 1933 K. These seven experiments are represented by smooth interpolated functions of specific heat and electrical resistivity, whose values are printed in Table 1 in 50 K increments. Deviations of individual specific heat functions from the final resulting function are about ±1% at 400 K and 1700 K respectively, and about ±0.5% in the middle of the range. Similar, somewhat smaller deviations were observed for electrical resistivity functions.

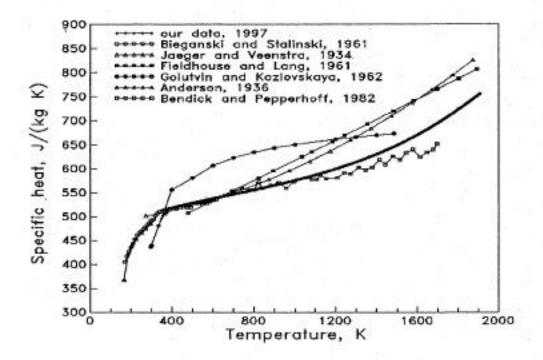


Figure 1. Specific heat of vanadium

## 3.1. Specific heat

Fig. 1 presents our specific heat data, together with low-temperature data of Bieganski and Stalinski [6] and Anderson [7], and the data above room temperature of Fieldhouse and Lang [9], Golutvin and Kozlovskaya [10] and Bendick and Pepperhoff [11]. Two low-temperature data sets reaching room temperature obtained by adiabatic calorimetry are in perfect agreement with each other. For this presentation only data above 160 K are shown. Our function joins smoothly to these data at their maximum temperature (340 K). Bendick and Pepperhoff [11] data obtained by high temperature

adiabatic calorimetry start at 335 K somewhat lower, to join our function at 367 K, staying in close agreement with it to 1125 K. Above that temperature they start to fall below ours, departure reaching 6,3% at their maximum temperature of 1690 K. For readability of the diagram in Fig. 1, all Bendick and Pepperhoff data [11] have not been shown; interval between individual data points was increased to approximately 20 to 30 K. Two data sets by Jacger and Veenstra [8], and Fieldhouse and Lang [9], computed from measured enthalpy data obtained by method of mixtures (metal-block calorimetry), start off from our function, following either linear [9], or mild parabolic function [8], often met in drop calorimetry specific heat data. Both sets reach their maximum values at 1880 K, some 10% above our function. Data of Golutvin and Kozlovskaya [10], also obtained by metal-block drop calorimetry differ from the rest.

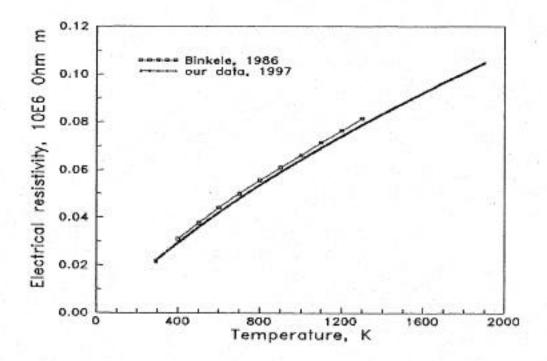


Figure 2. Electrical resistivity of vanadium

# 3.2. Electrical resistivity

Electrical resistivity function is shown in Fig. 2, together with the function of Binkele [12], the only other data set found. Beside the mean electrical resistivity function obtained by averaging results of individual experiments, electrical resistivity was measured at the room temperature using stationary state four-probe current reversal method [4,5] before beginning and after the end of pulse experiments. All our electrical resistivity data are presented in Table 1. The room temperature electrical resistivity value provided by the manufacturer<sup>3</sup> is also presented in Table 1. Not having own thermal expansion data, electrical resistivity was not corrected for this effect.

Comparison of the electrical resistivity value given by the manufacturer of 19.6  $\mu\Omega$ cm at 373,15 K with our measurement before pulse experiments effected at the same

<sup>&</sup>lt;sup>3</sup> Goodfellow, Cambridge, UK.

temperature of 21.33  $\mu\Omega$ cm (Table 1), indicates that the sample was not initially in an annealed state.

Gradual shift of individual electrical resistivity functions from experiment to experiment, confirmed by the stationary state four-probe electrical resistivity measurement at room temperature of 21,98  $\mu\Omega$ cm, giving difference of 3% between electrical resistivity measurements before and after the pulse experiments, suggests that pulse experiments, with their high heating- and relatively fast cooling rates induce change of electrical resistivity.

It is interesting that Binkele's function [12] lies above ours between 5.8% and 3.44%, biggest difference being at 400 and smallest at 1300K, although vanadium used in both studies was purchased from the same manufacturer, of the same nominal purity.

# 3.3 Emissivity

Data collected during high temperature experiments enabled determination of both hemispherical total emittance and the normal spectral emissivity. Hemispherical total emittance was determined in the range 1300 to 1900 K. The hemispherical total emissivity function is represented by

$$a_h = 0.06798 + 9.6154 \cdot 10^{-5} T (K)$$

From data simultaneously collected from a thermocouple and an optical pyrometer, in the range where measurements with these two detectors overlapped, normal spectral emissivity was computed according to the procedure detailed in [5]. Obtained normal spectral emissivity data are represented by

$$\varepsilon_{\lambda} = 0.26011 + 1.5625 \cdot 10^{-5} T (K)$$

Both the hemispherical total- and the normal spectral emissivity data are presented in Table 1.

### 3.4 Measurement uncertainties

Estimation of maximum uncertainties in the specific heat and electrical resistivity measurements by this method are given in [5], and they amount to 3% and 1%, respectively. The uncertainties reach their maximum values as the upper and the lowest limits of the measurement range are approached. Uncertainty is lowest typically in the region about 150 K from both ends of the measurement range.

Typical uncertainty in the hemispherical total emittance and normal spectral emittance is about  $\pm 5\%$  [5], which can be higher as the lowest temperature limit is approached.

Table I Numerical values of interpolated functions of specific heat, electrical resistivity, hemispherical total- and normal spectral emissivity of vanadium at 50 K intervals

(K)	(J kg <sup>-1</sup> K <sup>-1</sup> )	ρ (μΩ m)	En	$\mathcal{E}_{\lambda}$
293.15		0.2133*	-	K 2
293.15		0.2198**		
350	513.5	0.2592	-	-
400	518.6	0.2929	2	2
450	523.6	0.3258	-	-
500	528.4	0.3580		
550	533.1	0.3894	-	-
600	537.6	0.4200		-
650	542.2	0.4500		-
700	546.7	0.4793	4.5	- 23
750	551.2	0.5080		70
800	555.8	0.5360	× -	7.0
850	560.5	0.5634		2
900	565.3	0.5903	-	- 4
950	570.3	0.6166		
1000	575.5	0.6424	-	-
1050	581.0	0.6678		
1100	586.8	0.6926		
1150	592.9	0.7170		¥0
1200	599.5	0.7410		
1250	606.4	0.7646	2	2
1300	613.8	0.7879	0.193	0.280
1350	621.7	0.8107	0.198	0.281
1400	630.1	0.8333	0.203	0.282
1450	639.2	0.8556	0.207	0.283
1500	648.8	0.8776	0.212	0.283
1550	659.1	0.8994	0.217	0.284
1600	670.1	0.9210	0.222	0.285
1650	681.9	0.9424	0.227	0.286
1700	694.4	0.9636	0.231	0.287
1750	707.7	0.9847	0.236	0.287
1800	721.9	1.0057	0.241	0.288
1850	737.0	1.0266	0.251	0.289
1900	753.1	1.0475	0.255	0.290

<sup>\*</sup> The room temperature value obtained using the four-probe method with current reversal, measured before the first experiment.

<sup>\*\*</sup> The room temperature value obtained using the four-probe method with current reversal, measured after the final experiment.

## 4. DISCUSSION

Use of PtRh10%/Pt thermocouples instead of W5%Rh/W25%Rh thermocouples (which are usually employed in the high temperature millisecond resolution pulse calorimetry) improved accuracy of obtained results, although reducing thus the maximum operating temperature. In considering compromise between the two, advantage was given to the accuracy.

Insight into all available specific heat data sets, taking into account experimental techniques involved as well as their convenience or disadvantages for particular temperature regions, leads to a conclusion that our results, obtained with a method suited for the whole temperature range from room to 1900 K, contributed to better knowing of specific heat of vanadium.

Electrical resistivity results showed, in addition to dependence on thermal history, influence of exposing vanadium to pulse experiments. Compared with other available data set [12], our results confirmed the character of its temperature dependence and provided extension of the property function, particularly in the highest temperature region above 1300 K.

## ACKNOWLEDGEMENT

The research reported in this paper was funded by the Serbian Ministry for Science and Technology. Support is gratefully acknowledged.

Authors acknowledge with thanks contribution of Prof. Michel Laurent, Institut National des Sciences Apliquees de Lyon (CETHIL-INSA) France, who provided the vanadium sample for this study.

Provision of valuable information on the literature data relevant for this study by the THERSYST data bank is gratefully appreciated.

# REFERENCES

- N.Lj. Perović, K.D. Maglić and G.S. Vuković, Int. J. Thermophys. 17 1047-1055 (1996)
- K.D. Maglić, N.Lj. Perović, G.S. Vuković and Lj.P. Zeković, Int. J. Thermophys. 15 963-972 (1994)
- K.D. Maglić, N.Lj. Perović and G.S. Vuković, High Temp.-High Press. 29, 97-102 (1997)
- A.S. Dobrosavljević and K.D. Maglić, High Temp.-High Press. 21 411-421 (1989)
- K.D. Maglić, A.S. Dobrosavljević, N.Lj. Perović, A.M. Stanimirović, and G.S. Vuković, High Temp.-High Press. 27/28, 389-402 (1995/1996)
- Z. Bieganski and B. Stalinski, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 9(5), 367-72, (1961)
- C.T. Anderson, J. Am. Chem. Soc. 58, 564-6 (1936)
- 8. F.M. Jaeger, and W.A. Veenstra, , Rec. Trav. Chim. 53, 6777-87, 1934
- 9. I.B. Fieldhouse and J.I. Lang, WADD TR 60-904, 1-119 [AD268304] (1961)
- Yu.M. Golutvin and T.M. Kozlovskaya, Zh. Fiz. Khim., 36 (2), 362-4 (1962)
- W. Bendick and W.Pepperhoff, J. Phys. F 12, 1085-90 (1982)
- L. Binkele, High Temp.-High Press. 18, 599-607 (1986)